

SOLID CARBON DIOXIDE (DRY ICE)  
(Revised to October 1, 1944)

Solid carbon dioxide compressed into cakes is being manufactured for use as a refrigerant and sold under several trade names. These cakes of compressed solid carbon dioxide closely resemble packed snow in appearance and have a temperature of  $-109^{\circ}\text{F}$  ( $-78.5^{\circ}\text{C}$ ) or lower. Carbon dioxide at room temperatures and atmospheric pressure is a colorless, odorless gas. It occurs in the atmosphere to the extent of about 0.03 percent by weight, is a product of combustion and respiration, and a by-product of fermentation and of many chemical processes. It can exist as a solid at atmospheric pressure only because of its very low temperature. The cakes are made by compressing in a mold carbon dioxide snow produced by expanding liquid carbon dioxide at a low temperature from a high pressure to atmospheric pressure. In the expansion, part of the liquid is changed to a solid in the form of snow; the rest becomes a gas which is returned to the compressor for recompression and the making of more snow.

Carbon dioxide is different from water and most other substances in that it cannot exist as a liquid at atmospheric pressure ( $14.7 \text{ lb/in}^2$ )\*. Only when the pressure is equal to or greater than  $75.1 \text{ lb/in}^2$  (5.1 normal atmospheres) and its temperature  $-70^{\circ}\text{F}$  ( $-56.6^{\circ}\text{C}$ ) or higher (the "triple point" pressure and temperature) can carbon dioxide exist as a liquid. Hence instead of melting to a liquid as ice does, solid carbon dioxide passes directly from the solid to the gaseous state. This is one of the great advantages of solid carbon dioxide when used as a refrigerant. It does not wet spaces, packages, and materials refrigerated with it, and all the inconveniences due to the water from melting ice are avoided, provided moist air is excluded.

Density: The density of the commercial product depends upon the pressures applied in compressing the loose solid into cakes, and possibly on the manner of compressing it. A sample tested at the National Bureau of Standards weighed  $79 \text{ lb/ft}^3$ , or  $1.27 \text{ g/cm}^3$ ,

\*An excellent discussion of this subject by C.H. Meyers has been published in "Ice and Refrigeration". See "Carbon Dioxide in the Solid, Liquid and Vapor States", vol. 76, p. 535-37, 1929.

which may be compared with 57 lb/ft<sup>3</sup> or 0.92 g/cm<sup>3</sup> for ordinary ice. Crystalline carbon dioxide made by freezing liquid carbon dioxide weighs about 96 lb/ft<sup>3</sup>, or 1.53 g/cm<sup>3</sup>, (International Critical Tables, vol. I, p. 112 and vol. III, p. 43).

Temperature: The temperature of solid carbon dioxide surrounded by pure, gaseous carbon dioxide at a pressure of one normal atmosphere is -109°F, or -78.5°C, (International Critical Tables, vol. III, p. 207). In contact with air, its temperature is lower because the partial pressure of carbon dioxide gas is less. In contact with quiescent dry air a temperature of -114°F has been observed and in air currents even lower temperatures are observed.

Vapor Pressure: Pure solid carbon dioxide inclosed in a container in contact with its own vapor exerts a pressure, known as the vapor pressure, which varies with the temperature of the solid. The following table, which is a correlation\* of various data, shows the variation of the vapor pressure of carbon dioxide with temperature.

<u>Temperature</u> °F	<u>Absolute Pressure</u>		<u>Temperature</u> °C
	<u>Lb/in<sup>2</sup>.</u>	<u>Normal Atmospheres</u>	
-69.8	75.1	5.11	-56.6
-75	61.8	4.20	-59.4
-80	50.8	3.46	-62.2
-85	41.6	2.83	-65.0
-90	33.9	2.31	-67.8
-95	27.5	1.87	-70.6
-100	22.2	1.51	-73.3
-105	17.9	1.22	-76.1
-110	14.2	0.97	-78.9
-120	8.9	0.61	-84.4
-130	5.4	0.37	-90.0
-140	3.2	0.22	-95.6

---

\* BS J. Research 10, 381(1933)RP538

The normal atmosphere is defined as the pressure exerted by a column of mercury 76cm high under standard conditions (density 13.5951 g/cm<sup>3</sup>, acceleration of gravity 980.665 cm sec<sup>-2</sup>) and is very closely equal to a pressure of 14.7 lb/in<sup>2</sup>.

Latent Heat of Sublimation: In passing from the solid to the gaseous state at atmospheric pressure carbon dioxide takes up 248 Btu of heat energy per pound, or 138 cal/g, (International Critical Tables, vol. V, p. 138). A Btu (British Thermal Unit) is by definition the quantity of heat energy required to raise the temperature of one pound of water 1°F.

Latent Heat of Fusion: In passing from the solid to the liquid state at its "triple point" (-70°F, or -56.6°C) carbon dioxide takes up 82 Btu of heat energy per pound, or 45.3 cal/g (International Critical Tables, vol. V, p. 131).

Specific Heats of Solid and Gaseous Carbon Dioxide at Low Temperatures: The specific heat of solid carbon dioxide at -109°F (-78.5°C) is 0.31 Btu per pound degree fahrenheit or calorie per gram degree centigrade; that is, in order to raise or lower the temperature of one pound of solid carbon dioxide 1°F at -109°F, 0.31 Btu of heat energy has to be added to or taken from the solid, accordingly as its temperature is to be raised or lowered (International Critical Tables, vol. V, p.95). In the temperature interval between -109°F (-78.5°C) and +32°F (0°C) the mean specific heat of the vapor is about 0.19 Btu per pound degree fahrenheit or calorie per gram degree centigrade. Therefore one pound of carbon dioxide vapor after subliming from the solid will absorb 0.19 Btu for each degree rise in temperature between -109°F and +32°F (International Critical Tables, vol. V, p. 80).

Refrigerating Effect: Besides the refrigerating effect due to the change of state, there is the additional refrigerating effect of 27 Btu per pound at 32°F (15 cal/g at 0°C) equal to the amount of heat which the cold carbon dioxide vapor at -109°F (-78.5°C), after subliming from the solid, absorbs in being warmed to 32°F (0°C).



Hence one pound of carbon dioxide absorbs 275 Btu, or 153 cal/g, in changing from a solid at  $-109^{\circ}\text{F}$  ( $-78.5^{\circ}\text{C}$ ) to a gas at  $32^{\circ}\text{F}$  ( $0^{\circ}\text{C}$ ). This is approximately equal to twice the amount of heat, 144 Btu per pound or 79.5 cal/g absorbed by ice on melting at  $32^{\circ}\text{F}$  ( $0^{\circ}\text{C}$ ); and, as this is often expressed, one pound of solid carbon dioxide has approximately the same refrigerating effect at  $32^{\circ}\text{F}$  as two pounds of ice.

Mixtures of ice and salt are used to produce temperatures below  $32^{\circ}\text{F}$  and to refrigerate spaces at temperatures below those obtainable with ice alone. The heat absorbed by a pound of a mixture of ice and salt when the ice melts and the salt dissolves - its refrigerating effect - is smaller than the heat absorbed by one pound of ice, inasmuch as a pound of the mixture contains less than a pound of ice, the salt affecting the result only to a comparatively small extent. Moreover, the latent heat of fusion of ice is smaller at lower temperatures than it is at  $32^{\circ}\text{F}$ , and some of the ice is melted in cooling the mixture of ice and salt to the reduced temperature. These effects lower somewhat the amount of refrigeration which can be obtained from ice when it is used with salt. Hence, the ratio of the refrigerating effect of solid carbon dioxide to that of ice used with salt is greater than the ratio of their refrigerating effects when ice is used alone.

As solid carbon dioxide is ordinarily used as a refrigerant, the cold carbon dioxide gas as it sublimates from the solid displaces from the space to be refrigerated first the air and then the warm carbon dioxide gas. Gaseous carbon dioxide is a better heat insulator than air, the ratio of the heat conducted by carbon dioxide to that conducted by air under the same conditions at  $32^{\circ}\text{F}$  being 0.6. The heat, however, that passes from a warm exterior into a refrigerated space depends, among other things, upon the insulating properties and upon the thickness of the separating walls as well as upon the thermal conductivity of the gas inside. The better the heat insulation of the separating walls, the relatively less important is the thermal conductivity of the gas inside.

Uses: Solid carbon dioxide has been used most extensively for refrigerating ice cream in transit. It is also used for refrigerating shipments of other perishable commodities\*. In laboratories it

\*Carbon dioxide atmospheres have been found to produce harmful effects on living things kept in them. For this reason carbon dioxide atmospheres exercise a preservative action on meats and fish by impeding the growth of bacteria in them (See "Carbon Dioxide Preservation of Meat and Fish", by D.H. Killeffer, Industrial and Engineering Chemistry; vol. 22, p. 140-43(1930)). Since fruits, even after they are picked from the plant, are living things which take up oxygen and give off carbon dioxide, high concentrations of carbon dioxide in an atmosphere, in which they are stored, for short times or smaller

concentrations for longer times are harmful to some fruits. For further information on this subject, the reader is referred to the Bureau of Plant Industry, Department of Agriculture, Washington 25, D.C.

-----

is used to some extent for the production and maintenance of low temperatures for testing and experimental work.

Hazards: The obvious danger in handling solid carbon dioxide is that of freezing the hands or other portions of the body which may come into contact with the solid. Gloves should be worn or the material handled with tongs. Another danger is the possibility of illness or asphyxiation caused by breathing air which contains a high concentration of gaseous carbon dioxide. According to the International Critical Tables, vol. II, p. 319, the maximum safe concentration is two to three percent. Six to eight percent will cause dangerous illness in one-half to one hour. Since carbon dioxide vapor can exert a high pressure, if confined in a sealed container, there is danger of violent rupture.

Machinery for Making Solid Carbon Dioxide: The names and addresses of some companies which manufacture machinery used in the production of solid carbon dioxide are given below in alphabetical order.

- (1) Carbondale Machinery Co., Carbondale, Pa.
- (2) Frick Co., Inc., Waynesboro, Pa.
- (3) Vilter Manufacturing Co., Milwaukee, Wis.
- (4) Wittenmeier Refrigerating Co., Chicago, Ill.
- (5) York Ice Machinery Corporation, York, Pa.

References: A recent book, which deals extensively with solid carbon dioxide and contains many references to the literature, is "Carbon Dioxide" by Quinn and Jones, Reinhold Publishing Corporation, 330 West 42d Street, New York, N.Y. Articles, too numerous to list, dealing with various phases of the manufacture and use of solid carbon dioxide as a refrigerant, have been published in the following journals. Those interested in the manufacture and use of this refrigerant are referred to these journals beginning with the year 1930.

<u>Name of Journal</u>	<u>Publisher</u>	<u>Address</u>
1. Refrigerating Engineering	American Society of Refrigerating Engineers	37 West 39th St., New York, N.Y.
2. Refrigerating World	The Ice Trade Journal Co.	Woolworth Bldg., New York, N.Y.
3. Ice & Refrigeration	Nickerson & Collins Co.	5707 W. Lake St., Chicago, Ill.
4. Refrigeration	Refrigeration Publishing Co.	713 Glenn St., Atlanta, Ga.
5. The Ice Cream Review	The Olson Publishing Co.	5th & Cherry Sts. Milwaukee, Wis.
6. The Ice Cream Trade Journal	Thomas D. Cutler	171 Madison Ave., New York, N.Y.
7. Industrial and Engineering Chemistry	American Chemical Society	Mills Building, Washington, D.C.